JP 04-304465 Amano et al. 10-27-1992

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#### Notes:

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- 2. Texts in the figures are not translated and shown as it is.

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### [Document Name] Description

[Title of the Invention] The photo conductor for electronic photographs

## [Claim(s)]

[Claim 1] It is the photo conductor for electronic photographs characterized by having a photosensitive layer on a conductive base and a photosensitive layer containing the amine compound of a general chemical formula (I) as an electric charge transportation substance. [Chemical formula 1]

(In the inside A of a formula, the heterocyclic machine containing at least one kind of atom in a nitrogen atom, an oxygen atom, and a sulfur atom which is not replaced [ substitution or ] is expressed, and R1, R2, R3, and R4 express the alkyl group which is not replaced [ substitution or ], an aryl group, or an aromatic heterocycle machine, respectively.)

[Claim 2] In a photo conductor according to claim 1, the amine compounds of a general chemical formula (I) are R1, R2, R3, and R4. It is CH3, respectively. Photo conductor for electronic photographs characterized by being a machine.

[Claim 3] In a photo conductor according to claim 1, the amine compounds of a general chemical formula (I) are R1 and R2. It is CH3, respectively. A machine, R3, and R4 It is C2 H5, respectively. Photo conductor for electronic photographs characterized by being a machine.

[Claim 4] In a photo conductor according to claim 1, the amine compounds of a general chemical formula (I) are R1 and R2. It is CH3, respectively. A machine, R3, and R4 Photo conductor for electronic photographs characterized by being a phenyl group, respectively.

[Claim 5] In a photo conductor according to claim 1, the amine compounds of a general chemical formula (I) are R1 and R2. It is C2 H5, respectively. A machine, R3, and R4 It is CH2-C6 H5, respectively. Photo conductor for electronic photographs characterized by being a machine.

[Claim 6] It is the photo conductor for electronic photographs characterized by having a photosensitive layer on a conductive base and a photosensitive layer containing the amine compound of a general chemical formula (II) as an electric charge transportation substance. [Chemical formula 2]

(In the inside A of a formula, the heterocyclic machine containing at least one kind of atom in a nitrogen atom, an oxygen atom, and a sulfur atom which is not replaced [ substitution or ] is expressed, and R5 and R6 express the alkyl group which is not replaced [ substitution or ], an aryl group, or an aromatic heterocycle machine, respectively.)

[Claim 7] In a photo conductor according to claim 6, the amine compounds of a general chemical formula (II) are R5 and R6. It is CH3, respectively. Photo conductor for electronic photographs characterized by being a machine.

[Claim 8] In a photo conductor according to claim 6, the amine compound of a general chemical formula (II) is R5. CH3 A machine and R6 C2 H5 Photo conductor for electronic photographs characterized by being a machine.

[Claim 9] In a photo conductor according to claim 6, the amine compound of a general chemical formula (II) is R5. CH3 A machine and R6 Photo conductor for electronic photographs characterized by being a phenyl group.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the photosensitive layer of the photo conductor for electronic photographs, especially relates to the photo conductor for electronic photographs with a new electric charge transportation substance.

[0002]

[Description of the Prior Art] As photosensitive materials of the photo conductor for electronic photographs (it is also called a photo conductor below), conventionally Inorganic light conductivity substances, such as selenium or a selenium alloy, What distributed inorganic light conductivity substances, such as a zinc oxide or a cadmium sulfide, in the resin binder, What distributed organic light conductivity substances, such as organic light conductivity substances, such as poly-N-vinylcarbazole or Pori vinyl ANTORASEN, a phtalo SHIANIN compound, or a screw azo compound, in the resin binder, the thing which carried out vacuum deposition, etc. are used.

[0003] Moreover, although the function to hold surface charge to a photo conductor in a dark place, the function to receive light and to generate an electric charge, and the function to receive light similarly and to convey an electric charge are required There is what is called a laminated type photo conductor that laminated the layer which carried out functional separation in what is called a monolayer type photo conductor that united and had these functions in one layer, maintenance of the surface charge in the layer and dark place which contribute mainly to electric charge generating, and the layer which contributes to the electric charge transportation at the time of optical acceptance. The Carlsson method is applied to the image formation by the electronic photograph method using these photo conductors, for example. Electrification according [the image formation in this method] to the corona discharge to the photo conductor in a dark place, It is carried out by fixing to base materials, such as paper of the toner image by formation of electrostatic latent images, such as a character of the manuscript to the electrified photo conductor surface top, and a picture, and the toner of the formed electrostatic latent image developed and developed, and re-use is presented with it after the photo conductor after toner image transfer performs electric discharge, removal of remains toner, optical electric discharge, etc.

[0004] Many application to the photo conductor of the optical conductivity organic compound which was excellent in electric charge transportation ability is proposed with advantages, such as flexibility, heat stability, and film formation nature, in recent years. As an oxadiazole compound, for example, a U.S. Pat. No. 3189447 Description, As a PIRAZORIN compound, various electric charge transportation materials are known by the JP,55-42380,B number, the JP,57-101844,A number, the JP,54-150128,A number, etc. as JP,S59-2023,B and a HIDORAZON compound.

[0005]

[Problem to be solved by the invention] As mentioned above, although an organic material had many strong points which are not in the charge of non-equipments, the present condition is that what fully satisfies all the characteristics simultaneously required of an electronic photograph photo conductor is not obtained, and the problem was in sensitivity and the characteristic at the time of repetition continuous use especially.

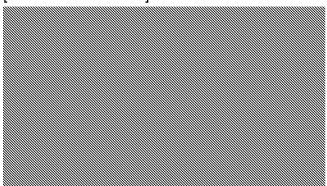
[0006] This invention is made in view of an above-mentioned point, and aims at offering the object for copying machines which excelled [sensitivity / high] in the characteristic repeatedly, and the photo conductor for electronic photographs for printers by using an organic new material which is not used for a photosensitive layer as an electric charge transportation substance until now.

[0007]

[Means for solving problem] According to this invention, the above-mentioned purpose has a photosensitive layer on a conductive base, and a photosensitive layer is attained by supposing that the amine compound of a general chemical formula (I) or a general chemical formula (II) is included as an electric charge transportation substance.

[8000]

## [Chemical formula 3]



[0009] (In the inside A of a formula, the heterocyclic machine containing at least one kind of

atom in a nitrogen atom, an oxygen atom, and a sulfur atom which is not replaced [ substitution or ] is expressed, and R1, R2, R3, R4, R5, and R6 express the alkyl group which is not replaced [ substitution or ], an aryl group, or an aromatic heterocycle machine, respectively.)

[0010]

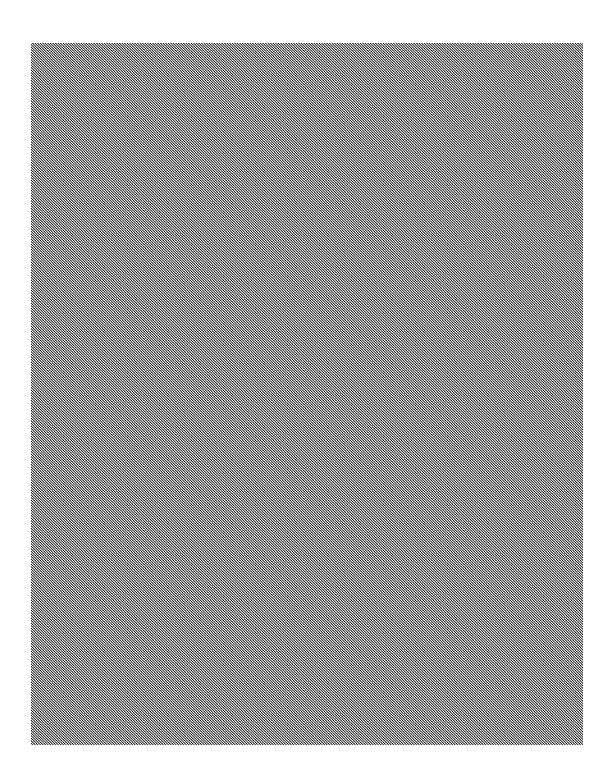
[Function] The example which used for the photosensitive layer the amine compound shown by said general chemical formula (I) or (II) is not known. In order that this invention persons may attain said purpose, while examining various organic materials wholeheartedly [ as a result of conducting much experiments on these amine compound, the technical elucidation has not been made enough yet, but ] Using the amine compound which has the specific frame shown by such said general chemical formula (I) or (II) as an electric charge transportation substance finds out that it is very effective in improvement in electrophotographic properties, and it came to obtain the photo conductor which excelled [ sensitivity / high ] in the characteristic repeatedly.

[0011]

[Working example] The example of the amine compound shown by said general chemical formula (I) used for this invention or (II) is shown in Table 1 - 8. As a chemical formula, it is the compound of I-1 to I-80 and II-1 - II-80.

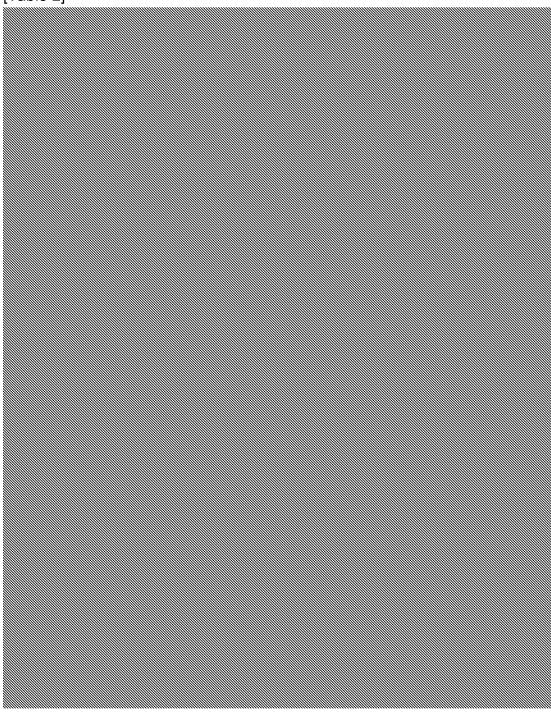
[0012]

[Table 1]



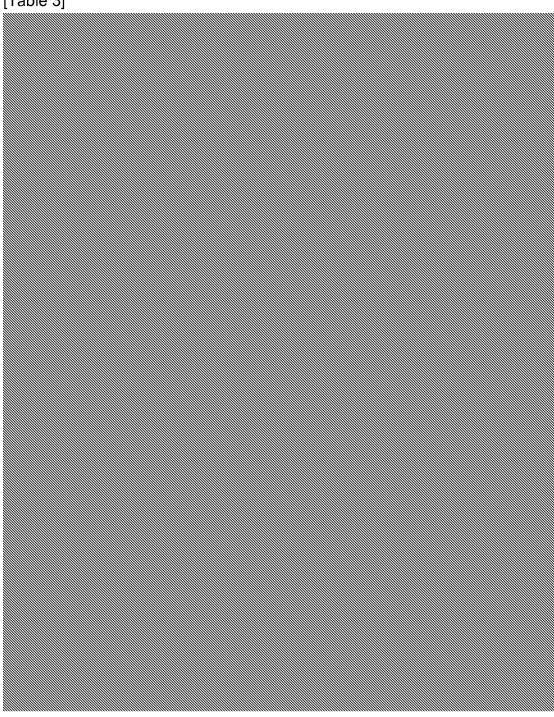
[0013]

[Table 2]



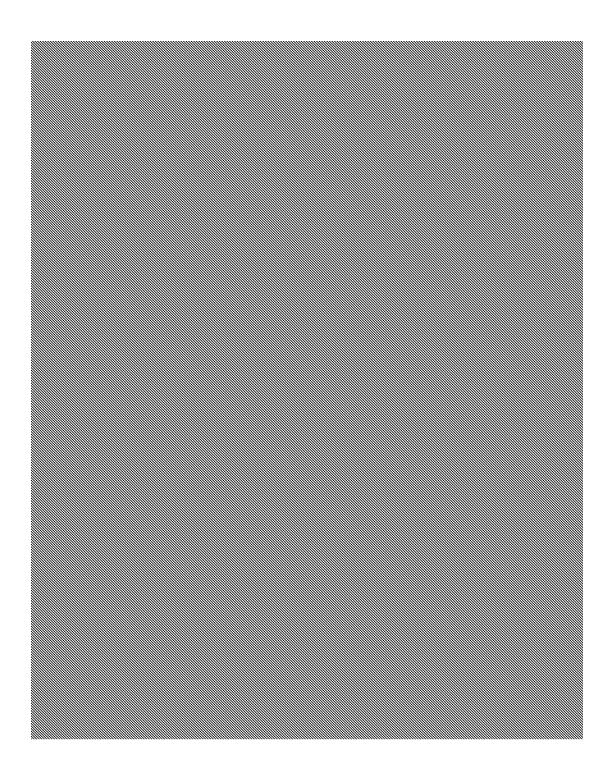
[0014]

[Table 3]



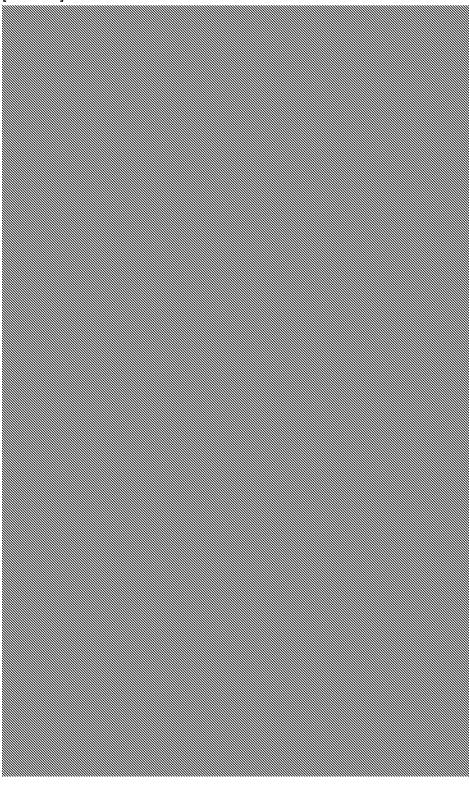
[0015]

[Table 4]



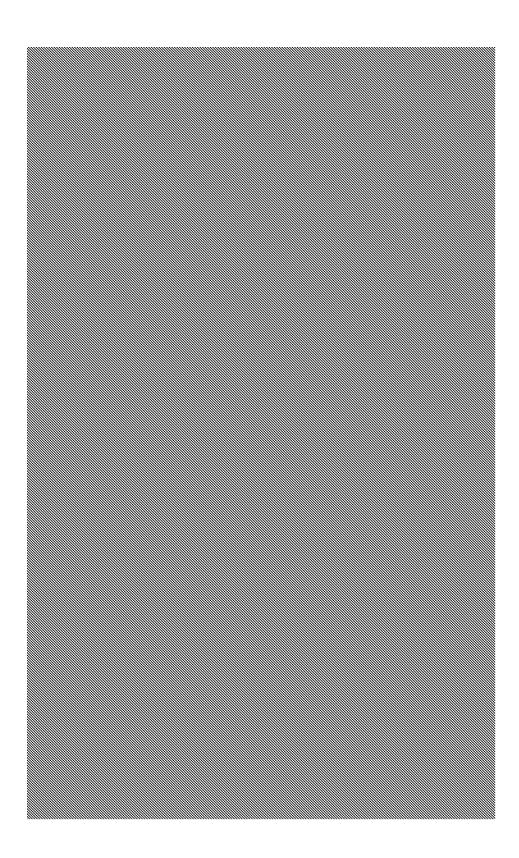
[0016]

[Table 5]



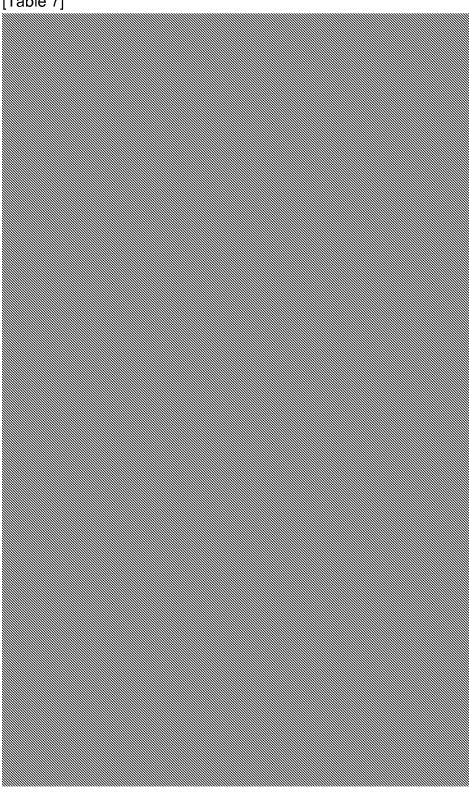
[0017]

[Table 6]



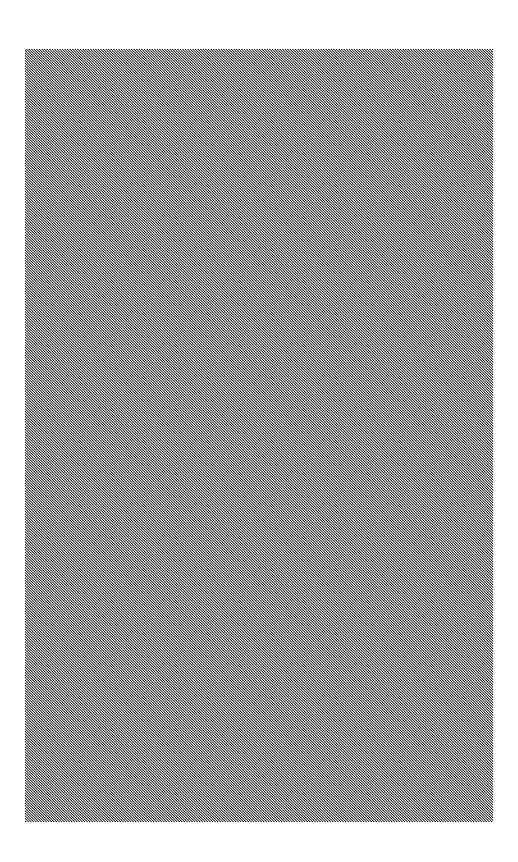
[0018]

[Table 7]



[0019]

[Table 8]



[0020] Next, it is as follows when the synthetic example of said compound is illustrated. [namely, the Gia Min compound of a chemical formula I-12 ] 2, 5-bis(4'-JIAMINO phenyl)-1, and 4-JICHIIN is added into iodine benzene, and it is obtained by performing the 4.2 time mol of materials amine for potassium carbonate, and performing the usual post-processing for the end of copper powder further, the amount of catalysts, in addition after carrying out heating flowing back. Moreover, the amine compound of chemical-formula II-14 is obtained when 2-phenyl 5-aminophenyl 1 and 4-JICHIIN are added into iodine toluene, and the 2.1 time mol of materials amine is performed for potassium carbonate, and it performs the usual post-processing further, the amount of catalysts in addition after carrying out [ the end of copper powder ] heating flowing back. Furthermore, it is compoundable by the same method or a known method also about compounds other than the above-mentioned synthetic example.

[0021] Although the photo conductor of this invention makes the above amine compounds contain in a photosensitive layer, as shown in drawing 1, drawing 2, or drawing 3, it can be used by the method of application of these amine compound.

[0022] drawing 1 - drawing 3 are the notional sectional views of the photo conductor of this invention -- 1 -- as for an electric charge generating layer and 5, a photosensitive layer and 3 are [ an electric charge transportation layer and 7 ] enveloping layers a conductive base, and 20, 21 and 22 an electric charge transportation substance and 6 an electric charge generating substance and 4.

[0023] The photosensitive layer 20 (composition usually called a monolayer type photo conductor) to which drawing 1 distributed the amine compound which are the electric charge generating substance 3 and the electric charge transportation substance 5 in the resin binder (binder) on the conductive base 1 is formed.

[0024] As for drawing 2, the photosensitive layer 21 (composition usually called a laminated type photo conductor) which consists of lamination with the electric charge generating layer 4 which makes the electric charge generating substance 3 a subject, and the electric charge transportation layer 6 containing the amine compound which is the electric charge transportation substance 5 is formed on the conductive base 1.

[0025] Drawing 3 is the thing of the reverse layer composition of drawing 2. In this case, in order to protect the electric charge generating layer 4, it is common to form an enveloping layer 7 further.

[0026] [ the Reason considered as two kinds of layer composition shown in drawing 2 and drawing 3 ] Even if it is going to use by a right electrification method by the layer composition of drawing 2 usually used as a negative electrification method, it is because it is required to have layer composition in which the electric charge transportation substance which suits this was not found yet therefore which was shown in drawing 3 at the present stage as a photo conductor of a right electrification method.

[0027] The photo conductor of drawing 1 makes an electric charge generating substance distribute in the solution which dissolved the electric charge transportation substance and the resin binder, and can be created by applying these dispersion liquid on a conductive base.

[0028] The photo conductor of drawing 2 can be created by applying the dispersion liquid which carried out vacuum deposition of the electric charge generating substance on the conductive base, or distributed and obtained the particles of the electric charge generating substance in the solvent or the resin binder, drying, applying the solution which dissolved the electric charge transportation substance and the resin binder on it, and drying.

[0029] [ the photo conductor of drawing 3 / the solution which dissolved the electric charge transportation substance and the resin binder ] It applies and dries on a conductive base, and the dispersion liquid which carried out vacuum deposition of the electric charge generating substance on it, or distributed and obtained the particles of the electric charge generating substance in the solvent or the resin binder are applied, and it dries, and can create by forming an enveloping layer further.

[0030] The conductive base 1 is the base material of other each layers simultaneously with the duty as an electrode of a photo conductor, any of cylindrical, tabular, and the shape of a film are sufficient, and what performed electric conduction processing on metal, such as aluminum,

stainless steel, and nickel, or glass, resin, etc. in quality of the material is sufficient as it.

[0031] As described above, the electric charge generating layer 4 applies the material which distributed the particles of the electric charge generating substance 3 in the resin binder, or is formed by methods, such as vacuum deposition, it receives light, and generates an electric charge. Moreover, the pouring nature to the electric charge transportation layer 6 and enveloping layer 7 of an electric charge which the electric charge generating efficiency is high, and simultaneously were generated is important, and it is desirable for pouring of a low electric field to have good electric field dependability few. As an electric charge generating substance, phtalo SHIANIN compounds, such as non-metal phtalo SHIANIN and titanylphthalocyanine, various azo, quinone, indigo paints Or dye, such as SHIANIN, squarylium, AZURENIUMU, and a PIRIRIUMU compound, selenium or a selenium compound, etc. is used, and a suitable substance can be chosen according to the light wavelength field of the exposure light source used for image formation. Since the electric charge generating layer should just have an electric charge generating function, the film thickness is decided from the optical absorption coefficient of an electric charge generating substance, generally is 5 micrometers or less, and is 1 micrometer or less suitably. The electric charge generating layer can also use an electric charge generating substance for this for an electric charge transportability substance etc. as a subject, adding to it. As a resin binder It is possible to use it, combining suitably a polymer, a copolymer, etc. of polycarbonate, polyester, polyamide, polyurethane, VCM/PVC, FENOKISHI resin, polyvinyl butyral, epoxy, diallyl phthalate resin, silicone resine, and methacrylic acid ester.

[0032] The electric charge transportation layer 6 is the coat which distributed the amine compound shown by said general chemical formula (I) or (II) as an organic electric charge transportability substance in a resin binder, the electric charge of a photo conductor is held as an insulator layer, and the function to convey the electric charge poured in from an electric charge generating layer at the time of optical acceptance is exhibited in a dark place. As a resin binder, a polymer, a copolymer, etc. of polycarbonate, polyester, polyamide, polyurethane, epoxy, silicone resine, and methacrylic acid ester can be used.

[0033] It is required to carry out neutralization disappearance of the surface charge in response to pouring of the electric charge which an enveloping layer 7 has the performance which penetrates the light which it has the function to receive and hold the electric charge of

corona discharge in a dark place, and an electric charge generating layer induces, penetrated light at the time of exposure, was made to reach an electric charge generating layer, and was generated. As covering material, organic insulation coat formation materials, such as polyester and polyamide, are applicable. these organicity material, glass resin, and SiO2 etc. -- the material which makes electrical resistance, such as a charge of non-equipments and also metal, and a metal oxide, reduce can also be mixed and used. [moreover, ] not being limited to an organic insulation coat formation material as covering material -- SiO2 etc. -- it is also possible to form the charge of non-equipments and also metal, a metal oxide, etc. by methods, such as vapor deposition and sputtering. In the wavelength field of the absorption maximum of the light of an electric charge generating substance, the thing of covering material transparent as much as possible is desirable as above-mentioned.

[0034] Although the film thickness of the enveloping layer itself is dependent also on combination composition of an enveloping layer, when repetition continuous use is carried out, it can be arbitrarily set up in the range out of which the bad influence of rest potential increasing does not come.

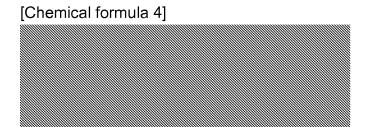
[0035] The amine compound 100 weight part shown with a work-example 1x type non-metal phtalo SHIANIN (H2 Pc) 50 weight part and said chemical formula I-1 [ solvent / a polyester resin (brand-name Byron 200: made by Toyobo) 100 weight part, and / tetrahydro franc (THF) ] It kneaded with the mixer for 3 hours, coating liquid was adjusted, and it applied by the wire bar method on the aluminum vapor deposition polyester film (aluminum-PET) which is a conductive base, and the photo conductor was created so that the film thickness after dryness might be set to 15 micrometers.

[0036] The coating liquid as for which the amine compound 80 weight part and polycarbonate resin (brand-name bread light L-1225: made in Teijin Chemicals) 100 weight part which are shown with the work-example 2 aforementioned chemical formula I-2 were dissolved and made to chlorination methylene is applied with a wire bar on an aluminum vapor deposition polyester film base. The electric charge transportation layer was formed so that the film thickness after dryness might be set to 15 micrometers. Thus, the titanylphthalocyanine (TiOPc) 50 weight part which carried out pulverization processing by the ball mill on the obtained electric charge transportation layer for 150 hours, It kneaded with the mixer for 3 hours with the polyester resin (brand-name Byron 200: made by Toyobo) 50 weight part, and

the THF solvent, coating liquid was adjusted, and it applied with the wire bar, and the electric charge generating layer was formed so that the film thickness after dryness might be set to 1 micrometer.

[0037] In work-example 3 work example 2, the electric charge transportation substance was changed into the amine compound shown with said chemical formula I-3 using the squarylium compound which changes into TiOPc and is shown with the following structural formula, and the photo conductor was produced like the work example 2.

[0038]



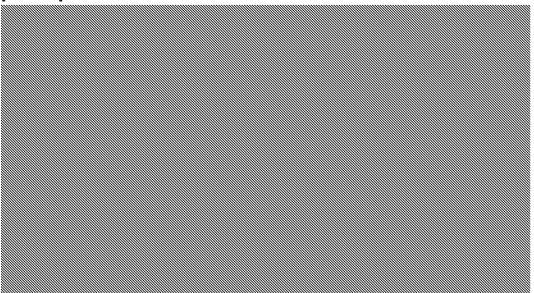
[0039] In work-example 4 work example 2, the electric charge transportation substance was changed into the amine compound shown with said chemical formula I-4 using the chloro DAIAN blue which is a screw azo pigment as changed into TiOPc, for example, shown in JP,47-37543,A, and the photo conductor was produced like the work example 2.

[0040] Thus, the electrophotographic properties of the obtained photo conductor were measured using the product electrostatic record paper test equipment made from the Kawaguchi electrical machinery "SP-428." The surface potential VS of a photo conductor (bolt) is the surface potential of the first stage at the time of performing +6.0kV corona discharge for 10 seconds in the dark place, and making it the photo conductor surface right-charged. Then,

the surface potential Vd (bolt) when carrying out dark place maintenance for 2 seconds, where corona discharge is stopped is measured, it continues further, the photo conductor surface is irradiated [ with an illumination of 2 luxs ], and it is Vd. It was referred to as half-attenuation light exposure E1 / 2 (looks and second) in quest of time (second) until it becomes half. Moreover, surface potential when glaring white light with an illumination of 2 luxs for 10 seconds was made into the rest potential Vr (bolt). Moreover, since the high sensitivity in long wavelength light was expectable about work examples 1-3, the electrophotographic properties when being with monochromatic light with a wavelength of 780nm were also measured simultaneously. namely, Vd \*\*\*\*\*\* -- the rest potential Vr (bolt) when this having measured similarly, glaring 1-microwatt monochromatic light (780nm) instead of white light next, and calculating a half-attenuation light exposure (muJ/cm2), and irradiating the photo conductor surface for 10 seconds was measured. A measurement result is shown in Table 9.

[0041]

# [Table 9]



[0042] There is no inferiority of 1, 2, 3, and 4 work examples in a half-attenuation light exposure and rest potential, and they show the good characteristic also with surface potential

so that it may see in Table 9. Moreover, in work examples 1-3, long wavelength light with a wavelength of 780nm also shows high sensitivity, and it turns out that it is usable enough as an object for semiconductor laser printers.

[0043] On an aluminum plate with a work-example 5 thickness of 500 micrometers, carry out vacuum deposition of the selenium to 1.5 micrometers in thickness, and an electric charge generating layer is formed. Next, the coating liquid as for which the amine compound 100 weight part and polycarbonate resin (PCZ200: made by Mitsubishi Gas Chemical) 100 weight part which are shown by chemical-formula II-1 were dissolved and made to chlorination methylene was applied with the wire bar, and the electric charge transportation layer was formed so that the film thickness after dryness might be set to 20 micrometers. In this photo conductor, VS =-650V, Vr =-25, E1 / 2 = 1.4 lux and a second, and the good result were obtained.

[0044] Knead a x type non-metal phtalo SHIANIN 50 weight part and a VCM/PVC copolymer (brand-name MR-110: made by Nippon Zeon) 50 weight part with a mixer with chlorination methylene like work-example 6 work example 2 for 3 hours, and coating liquid is prepared. On the aluminum base material, it applied so that it might be set to about 1 micrometer, and the electric charge generating layer was formed. Next, the amine compound 100 weight part shown by chemical-formula II-2, the polycarbonate resin (pan-light L-1250) 100 weight part, and the silicon oil 0.1 weight part were mixed with chlorination methylene, it applied so that it might be set to about 15 micrometers on an electric charge generating layer, and the electric charge transportation layer was formed. Thus, in the obtained photo conductor, VS =-680V, E1 / 2 = 1.1 lux and a second, and the good result were obtained.

[0045] In work-example 7 work example 6, the electric charge transportation substance was changed into the amine compound shown by chemical-formula II-3, using the screw azo pigment which changes into non-metal phtalo SHIANIN and is shown with the following structural formula, and the photo conductor was created like the work example 6. Thus, in the obtained photo conductor, VS =-630V, E1 / 2 = 1.7 lux and a second, and the good result were obtained.

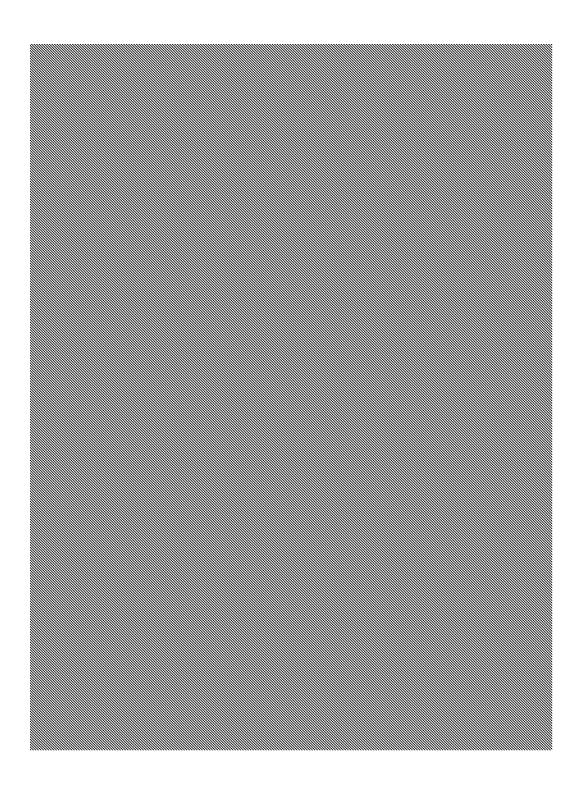
[0046]



[0047] work-example 8 chemical formula I-5 or a chemical formula I-80 and chemical-formula II-4 to chemical-formula II-80 -- the result which created the photo conductor like [ each ] the work example 4, and was measured using "SP-428" is shown in Table 10 and 11. Deed positive electrification of the +6.0kV corona discharge was carried out for 10 seconds in the dark place, and half-attenuation light exposure E1/2 at the time of glaring white light with an illumination of 2 luxs (looks and second) showed.

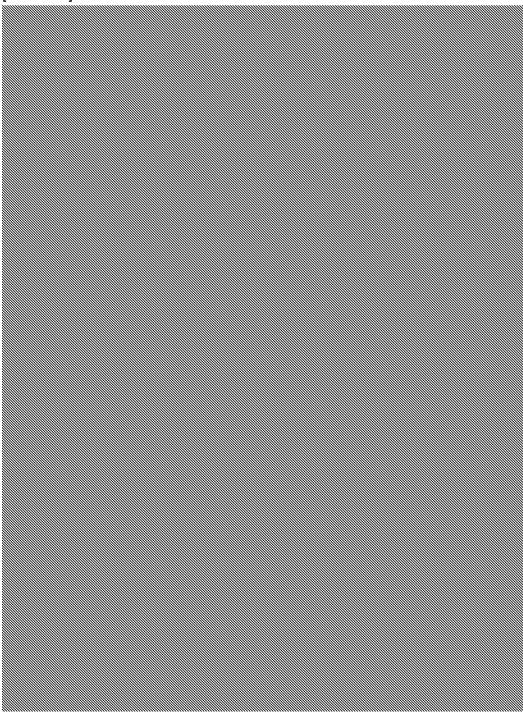
[0048]

[Table 10]



[0049]

[Table 11]



[0050] It is half-attenuation light exposure E1/2 also about the photo conductor using the amine compound shown by the amine compound shown with a chemical formula I-5 or a chemical formula I-80, chemical-formula II-4 to chemical-formula II-80 as an electric charge transportation substance so that it may see in Table 10 and 11. It was good.

[0051]

[Effect of the Invention] According to this invention, it can write with using the amine compound shown by said general chemical formula (I) or (II) as an electric charge transportation substance on a conductive base, and the photo conductor which moreover excelled [sensitivity / high] in the characteristic repeatedly also in right electrification and negative electrification can be obtained. Moreover, the electric charge generating substance can choose a suitable substance corresponding to the kind of exposure light source, and if an example is given and a phtalo SHIANIN compound, a squarylium compound, a screw azo compound of a certain kind, etc. will be used, it can obtain an usable photo conductor to a semiconductor laser printer. Furthermore, it is possible to install an enveloping layer in the surface if needed, and to improve endurance.

[Brief Description of the Drawings]

[Drawing 1] The sectional view showing the monolayer type photo conductor concerning the work example of this invention

[Drawing 2] The sectional view showing the laminated type photo conductor of negative electrification concerning the work example of this invention

[Drawing 3] The sectional view showing the laminated type photo conductor of right electrification concerning the work example of this invention

[Explanations of letters or numerals] 1 Conductive Base 3 Electric Charge Generating Substance 4 Electric Charge Generating Layer 5 Electric Charge Transportation Substance 6 Electric Charge Transportation Layer 7 Enveloping Layer 20 Photosensitive Layer 21 Photosensitive Layer 22 Photosensitive Layer	
[Translation done.]	